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EVIDENCE FOR "INCLINED" CO ON Pd(210)

BY

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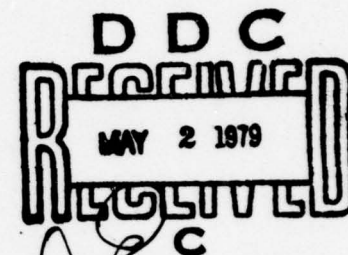1000 Berlin 33, W. Germany

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20. Abstract (continued)

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Evidence for "Inclined" CO on Pd(210)

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Abstract

The ESDIAD method (Electron Stimulated Desorption Ion Angular Distributions) has been used to verify an unusual bonding configuration for CO adsorbed on the rather open Pd(210) surface. In a previous infrared reflection-absorption study of CO on Pd(210) (where top layer atoms with the nearest neighbor distance of 2.73 Å do not exist) the results indicated that CO was bridge-bonded to two Pd atoms via the carbon atom. Such bridge-bonding can only occur in several distinct sites between atoms in the first and second atom layers, so that the axes of adsorbed CO molecules are expected to be inclined away from the normal by $\sim18°$. The ESDIAD data are consistent with the infrared observations at low coverages (two-fold symmetric triangular ESDIAD patterns dominated by off-normal ion emission in appropriate symmetry directions), but the results are more complex at higher coverages. At the saturation CO coverage at 90 K, the data indicate that CO is bonded normal to the surface. The relative yields of O^+ and CO^+ ions are sensitive to the bonding mode, with O^+ alone seen for bridge-bonded CO at low coverages and both O^+ and CO^+ ions observed at higher coverages.

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I. Introduction

In recent years, studies of the structure of adsorbed CO on metal surfaces have received much attention from surface scientists. Ultra-violet Photoemission Spectroscopy (UPS) and angular resolved UPS have been used to characterize the adsorption of CC on Ni(100)[1], Pt(111)[2], and Ru(001)[3]. In all three cases, the balance of evidence indicates that CO is molecularly bonded through the C atom with the CO axis perpendicular to the surface[4]. This result is analagous to the metal-ligand configuration in transition metal carbonyls such as Ni(CO)$_4$[5]. Recently, the Electron Stimulated Desorption Ion Angular Distributions (ESDIAD) method has also been used[6] to verify that CO is bonded perpendicular to the Ru(001) surface. There have also been reports of "inclined" CO on Ni(100)[7] and Cu(110)[8]; however, the evidence is less conclusive.

In several recent studies[9,10], the ESDIAD method has been shown to be useful in characterizing the structures of molecules adsorbed on surfaces. In general, there appears to be a correspondence between surface bond angles and ion desorption angles. In the present work, we report on the use of ESDIAD to verify an unusual bonding configuration for CO on the (210) surface of f.c.c. Palladium. In an infrared reflection-absorption study[11] of CO on Pd(210) and (100) the value of the C-O stretching frequency indicated that at low coverages CO was bridge-bonded to two Pd atoms via the C atom. The Pd(210) is a rather open surface and top layer atoms with the nearest neighbor distance of 2.73 Å do not exist (cf. Fig. 1); the shortest distance between top layer atoms is 3.88 Å in the [001] direction. Bridge bonding has not been reported to occur in transition metal carbonyls for metal-metal

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spacings greater than ~2.78 $\overset{\circ}{A}$[12]. On Pd(210 it would appear therefore that bridge-bonding could only occur on sites of the kind which exist between atoms in the first and second atom layers, so that the axes of adsorbed CO molecules are expected to be inclined away from the normal by ~18°.

The ESDIAD data confirm that the CO axis is inclined at low coverages, but the results are more complex at higher coverages. At the CO saturation coverage at 80 K, the data suggest that CO is bonded normal to the surface.

II. Experimental

The Pd(210) crystal used for these studies was prepared as described previously[11] and polished on one side only; the initial cleaning involved repeated cycles of Ar^+ ion bombardment, followed by annealing at temperatures up to 1000 K. At various times, a combination of Ar^+ bombardment, heating in oxygen, and vacuum annealing were found to be necessary to remove traces of P, C, S or O which appeared on the surface. The crystal was spot-welded to two short Pd leads and heated resistively; the temperature range employed in these studies was 80 K-1000 K, as measured using a W-3% Re vs W-26% Re thermocouple.

The apparatus used for the ESDIAD studies has been described previously[13]. ESDIAD and LEED patterns were observed on a phosphor screen using a display-type retarding grid analyzer. In addition, ESD ions could be measured using a quadrupole mass spectrometer. Surface cleanliness was characterized in situ using Auger electron spectroscopy. Temperature programmed desorption (TPD) measurements were made with the crystal facing the mass spectrometer so as to maximize the direct des-

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orption signal from the polished surface. By comparing the TPD spectra for the crystal in different positions, it is estimated that <u>at most</u>, the rear surface contributes about 25% of the observed signal.

III. Results

The CO/Pd(210) system was characterized using several different experimental methods, Temperature Programmed Desorption (TPD), Low Energy Electron Diffraction (LEED), ESDIAD, and ESD ion yields. Each of these will be discussed in turn, and related to the structure(s) of adsorbed CO.

A ball model of the Pd(210) surface is shown in Fig. 1, with the atop site labeled A, and with several potential bridge-bonding sites between atoms in adjacent layers labeled B to E. Note that the only potential bridge sites having the two-fold symmetry of the (210) sub-strate are sites of the type labeled B and E. The C sites have been previously suggested as potential bonding locations for adsorbed CO[11].

A series of TPD (also known as flash desorption) spectra for CO adsorbed on Pd(210) at ∿323 K are shown in Fig. 2. For exposures less than ∿2.5 L, a single peak is seen in each spectrum. This peak shifts slightly to lower temperatures as coverage increases. At higher ex-posures, a second state is observed to populate and reach saturation at an exposure of ∿6 L. We define the peak at ∿485 K to be associated with a binding state we call the β_2 state, and the peak at ∿390 K to be the β_1 state. We estimate the binding energies of these first order states using the Redhead[14] relationship

$$\frac{E_d}{RT_p} = \ln \frac{\nu_1 T_p}{\beta} - \ln \frac{E_d}{RT_p}$$

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where E_d is the desorption energy, T_p is the temperature at which the peak maximum occurs, R is the gas constant, β is the heating rate (11 to 8 K/s), and ν is the first order pre-exponential quantity, assumed to be 10^{13}/sec. The values of E_d are calculated to be 29.2 kcal/mol (121 kJ/mole) for the β_2 state and 23.2 kcal/mole (97 kJ/mol) for the β_1 state. Conrad et. al.[15] have reported a coverage-dependent desorption energy for CO on Pd(210) ranging from 34 kcal/mol at zero coverage to 25 kcal/mol near saturation coverage, but did not report two distinct peaks in the thermal desorption spectra. If we define the saturation coverage at 323 K as $\theta_s = 1$, the maximum coverage in the β_2 state ($\sim$2.5 L exposure) is $\theta_s \sim 2/3$ and the maximum coverage in the β_1 state ($\sim$8.0 L exposure) is $\theta_s \sim 1/3$. For adsorption of CO at 90 K the β_2 and β_1 states are also seen in TPD. In addition, at the highest coverages at 90 K, an additional (β_o) state is observed to desorb with $T_p \sim$230 K. The maximum coverage of the β_o state is roughly the same as the β_1 state. In all cases, the CO was observed to be reversibly, molecularly adsorbed; no evidence for dissociation was seen in these experiments.

The LEED pattern for the clean Pd(210) surface (fig. 3a) exhibits the expected symmetry and substrate spots without any evidence for re-construction or faceting, in agreement with previous work[11,15]. When the LEED pattern is compared with the crystal model (Fig. 1), there is a 180° ambiguity in the definition of the crystal orientation: although the [1$\bar{2}$0] azimuth contains a mirror plane, there is no two-fold rotational axis in the surface normal. A LEED intensity analysis could, in prin-ciple, resolve the orientation question, but as we shall discuss below, this ambiguity is removed by ESDIAD.

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Upon exposure to CO at either 300 K or 80 K, no extra features are observed until streaks appear in the [$1\bar{2}0$] directions (exposures >3 L); the streaks finally coalesce into half-order spots characteristic of a (1 x 2) surface structure (occasionally, evidence for a (1 x 3) structure is seen also). As suggested previously[11,15], CO at low coverages forms a (1 x 1) overlayer (the β_2 state). As the CO coverage increases, the weak streaks are indicative of ordered rows of molecules parallel to the [001] direction, with random separation of the rows in the [$1\bar{2}0$] direction. Further exposure to CO causes the streaks to coalesce into spots, indicating the presence of a coincidence lattice.

A sequence of ESDIAD patterns (both photographs and schematic patterns) corresponding to CO adsorption at 80 K is shown in Fig. 3b-3e; the direction of the surface normal is designated by +. The first three patterns (b,c,d) are substantially the same as those observed for corresponding CO exposures at 300 K, but the appearance of the patterns is "sharper" at 80 K than 300 K due to reduction of thermal effects such as bending vibrations[6], surface diffusion, etc. At low exposures ($\stackrel{\sim}{\scriptstyle\sim}$ 1.5 L, corresponding to $\theta_s \stackrel{<}{\scriptstyle\sim}$ 0.5) the ESDIAD pattern has the appearance of an arrowhead (Fig. 3b) which desorbs in an off-normal direction along the [120] azimuth, as defined by the LEED pattern. This observation of this pattern is consistent with bridge bonding of CO in sites of the type labeled B in Fig. 1, although the E sites cannot be eliminated. Such a bonding configuration would be expected to yield ionic fragments $\sim$18° away from the normal direction along the [120] azimuth. The polar desorption angle cannot be determined accurately due to distortion of the ion trajectories by the applied electric field[6,13] but comparison of this pattern with patterns having known

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ion desorption angles demonstrates that an angle of ∿18° is reasonable. Furthermore, the ambiguity regarding the registry of the LEED pattern with the structural model is removed. It appears, then, that at low CO coverages the β_2 state, the (1 x 1) LEED pattern, and the arrowhead ESDIAD pattern of Fig. 3b are all related to the adsorption of CO at two-fold bridge sites. This confirms the infrared results[11] in which the measured CO stretching frequency was consistent with bridge-bonded CO. The present results extend the i.r. data by specifying which of the many possible bridge sites on the (210) surface are occupied.

As the CO coverage increases, the ESDIAD patterns become more complex. For exposures $\gtrsim$ 2L (patterns 3c, 3d) new features appear. There is a hazy triangular background with two regions of maximum intensity: at the lower apex of the triangle, and along the base (top of patterns). The [1$\bar{2}$0] axis bisects the isosceles triangle. The center of the patterns are dark, indicating little or no ion emission normal to the surface. The pattern of Fig. 3d corresponds roughly to the pattern seen for saturation coverage at 300 K, when the β_1 TPD state is saturated. As will be discussed below, the dominant ESD ion contributing to Fig. 3b, c, d is O^+; at 80 K, only small CO^+ signals are seen in the range 3 to 5 L, at 300 K, no CO^+ is seen (cf. Fig. 4).

When the CO exposure is increased at 80 K, the CO coverage increases due to population of the β_o state. In addition, the triangular pattern of Fig. 3d converts to that of Fig. 3e; i.e., a circular beam which desorbs normal to the surface and contains contributions from both O^+ and CO^+. This suggests that one of several possiblities may be occurring at the highest CO coverages at 80 K, such as: (a) perhaps

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the bonding geometry is changed from largely bridge-bonded "inclined" CO to linear, normally-bonded CO as the additional CO is added to the surface, or (b) perhaps a linear form of CO is adsorbed in atop sites on the (210) surface, causing the ESD ion yield from the "inclined" CO to be blocked, or suppressed. We also note that the (1 x 2) LEED pattern does not display additional structure with increasing CO coverage at 80 K. Evidence for linearly-bonded CO was not seen in the reflection IR studies[11], perhaps due to the inability to make measurements below 300 K. It will be of interest to learn if the linear CO model will be confirmed in future low temperature IR studies.

Figure 4a shows the O^+ and CO^+ ion yields from the Pd(210) surface as a function of exposure to CO at 80 K. The electron beam was turned on intermittently during the experiment to minimize ESD damage to the adsorbed layer. Note that the O^+ signal rises to a maximum value at $\sim$ 3 L, and then decreases to a level value. An appreciable CO^+ signal does not appear until the surface is nearly saturated. Figure 4b shows the O^+ ion yield vs. CO exposure at 300 K. The signal rises as the β_2 state populates and passes through a maximum at 2.8 L, near the onset of population of the β_1 state. No CO^+ signal is seen following evacuation of the CO, although a small CO^+ signal is measured from the surface in equilibrium with gas phase CO at 1×10^{-8} torr.

IV. Discussion

The combination of the previous IR results[11] with the present ESDIAD, LEED, thermal desorption measurements, and ESD ion yields leads to the following model of CO adsorption on Pd(210). At low CO coverages,

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when only the β_2 state is present in a (1 x 1) array, CO is bridge-bonded and adsorbs mostly at B sites, inclined away from the normal (Fig. 1). Electron bombardment of bridge-bonded CO will result in desorption of O^+ ions, but little or no CO^+ yield. As the β_1 state populates, some of the adsorbed CO moieties move out-of-registry with the substrate, and changes are seen in LEED, ESDIAD, and in the O^+ ion yield. The lack of CO^+ at 300 K indicates that the CO is still multiply coordinated, although perhaps not in discrete sites. At the highest coverages at 80 K, the ESDIAD pattern is dominated by normal desorption and a substantial CO^+ ion yield is observed. Either the inclined CO is caused to "stand up straight" due to lateral CO-CO interactions, or the normally-bonded β_0 CO state blocks and suppresses the ESD ion yield from the inclined CO. The notion that both CO^+ and O^+ can be associated with linearly bonded CO is confirmed by recent ESD studies of linearly-bonded CO on Ru(001)[6,16].

Although the low and high coverage limits of CO adsorption can be readily characterized by "inclined" and "normal" CO, respectively, the intermediate coverage region is not so easily described. The arrowhead-like shape of the off-normal beam of Fig. 3b, the "extra" beam of Fig. 3c and 3d, and the hazy background of Figs. 3c and 3d remain to be interpreted. The most pronounced feature (the "extra" beam of 3c and 3d) corresponds to ion emission in an off-normal direction where simple bridge-bonding does not appear possible, on the basis of the structure in Fig. 1. It is tempting to suggest this may be an inclined linear CO species, but the absence of a CO^+ ESD signal at 300 K and the CO stretching frequency measured at high coverages suggest that only bridge-bonded species are present.

Possible explanations of the unusual features of patterns 3 b-d may lie in some structural and dynamic processes which have been reported in transition metal carbonyl chemistry. In addition to the linear and doubly bridging CO configurations discussed above, grossly unsymmetrical CO bridges have been reported[17]. In this arrangement, an M-C-O chain "leans" toward a neighboring metal atom, M'. The C...M' distance is short enough to imply some sort of bonding ($\sim$2.3 to 2.4 Å) while the M-C distance is of the usual length for an ordinary terminal group ($\sim$1.8 to 1.9 Å). The M-C-O angle is about 165° to 170°, and the $\frac{M'}{M}$>CO group is approximately planar. It is not unreasonable to suggest that such bonding can occur on the Pd(210) surface, particularly when the CO is "out-of-registry" with the substrate.

There is also evidence for stereochemical non-rigidity in some transition metal carbonyls. The term "fluxionality" is used to describe the scrambling of linear and bridged CO species[17]. The evidence for such dynamic rearrangements in carbonyls has been seen in a variety of ^{13}C NMR studies, and is well documented[17]. The possibility that analagous processes occur on surfaces is currently being explored in studies of the temperature dependence of the ESDIAD patterns[18]. It appears at present that some of the triangular hazy background, as well as the extra features of the ESDIAD patterns for CO on Pd (Fig. 3 c,d) may indeed originate in such structural and dynamical processes as unsymmetrical CO bridges and fluxionality.

V. Acknowledgments

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Figure Captions

Figure 1.   Model of Pd(210) surface, with possible bonding sites for CO labeled. The section view illustrates how the CO molecule is "inclined" in the B sites.

Figure 2.   Temperature programmed desorption (TPD) of CO from Pd(210). The partial pressure of CO, ΔP_{CO}, is plotted vs. crystal temperature (K). The curves are displaced arbitrarily for clarity. Adsorption temperature $T_{ads} \simeq 320$ K. CO exposures corresponding to each curve are

   (a) 1×10^{-6} Torr s
   (b) 2×10^{-6} Torr s
   (c) 3×10^{-6} Torr s'
   (d) 6×10^{-6} Torr s

Figure 3.   LEED and ESDIAD photographs and schematic patterns for CO on Pd(210). Adsorption temperature for CO was $T_{ads} = 80$ K.

   (a) LEED pattern of clean surface, $V_e = 100$ V
   (b)-(e) ESDIAD patterns for increasing CO exposures at 80 K. For each photo, total electron bombardment current $\sim 1 \times 10^{-7}$ A and electron energy ~ 300 eV. Exposures corresponding to each pattern were (b) 0.8×10^{-6} Torr s, (c) 3.4×10^{-6} Torr s, (d) 4.7×10^{-6} Torr s, (e) 8×10^{-6} Torr s.

Figure 4.   Plots of ESD ion yield (arbitrary units) as a function of CO exposure. Electron bombardment was intermittent to reduce ESD damage. Electron energy = 150 eV.

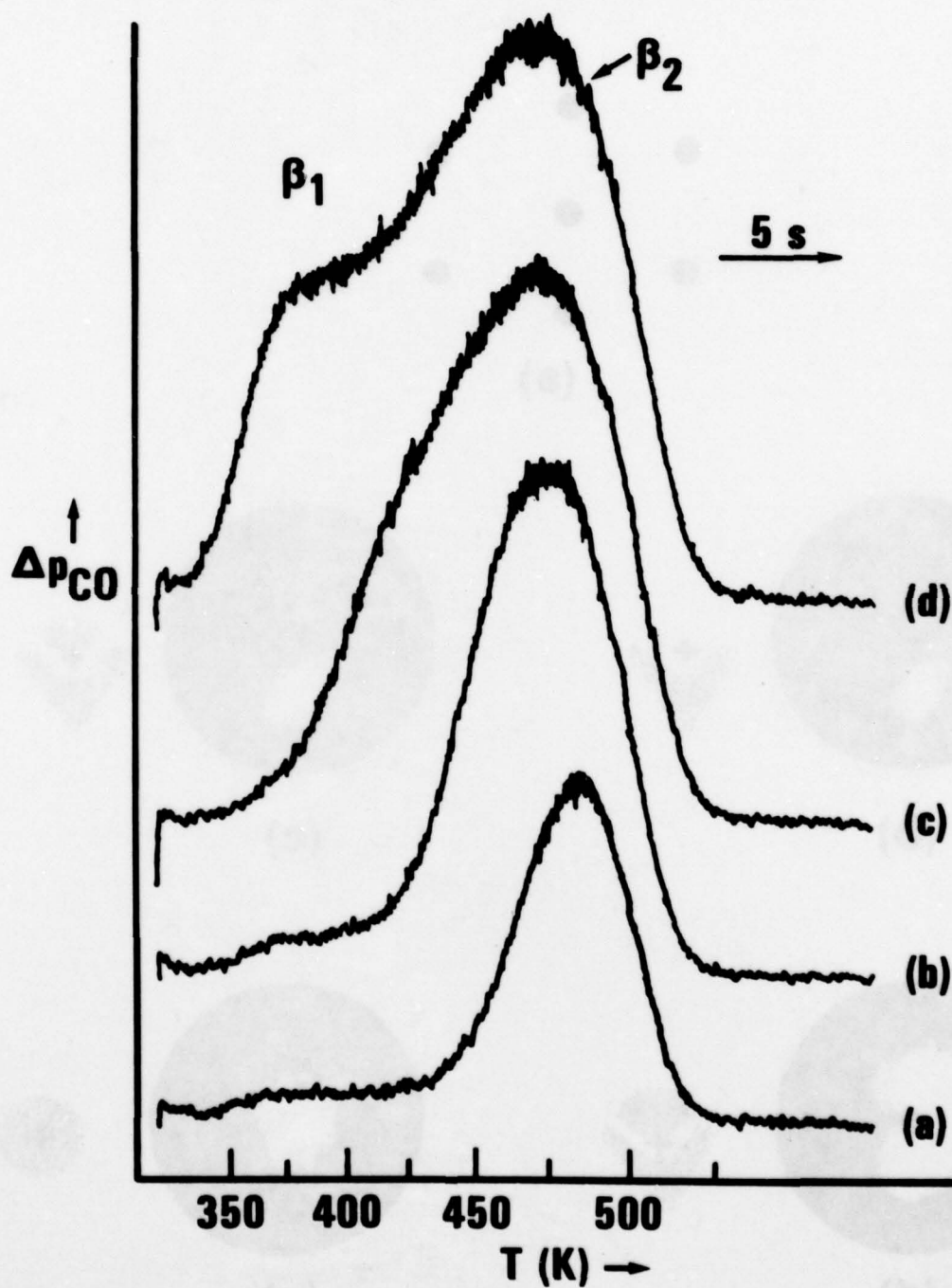Pd (210) Surface Showing Some Possible CO Bonding Sites
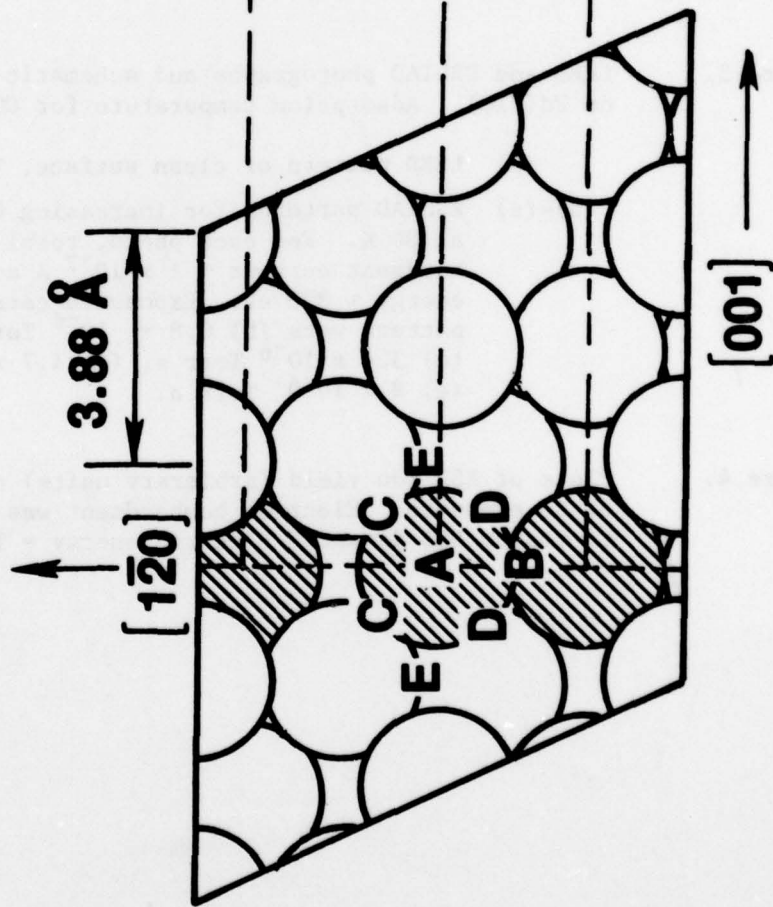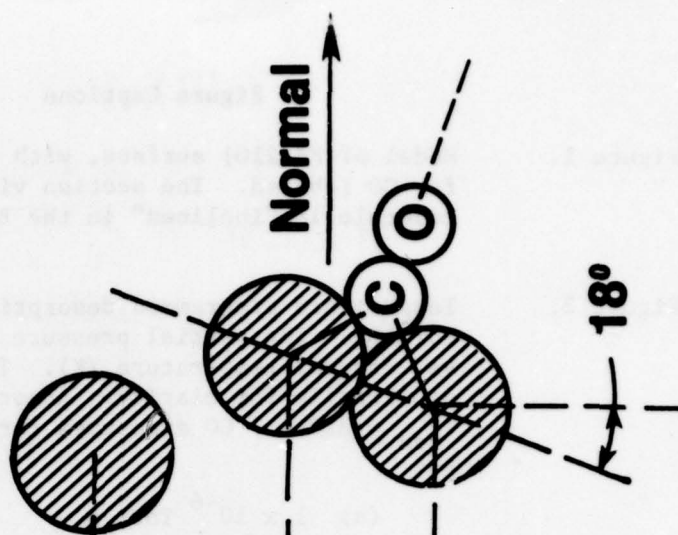
TEMPERATURE PROGRAMMED
DESORPTION OF CO
FROM Pd (210)

CO Adsorption on Pd (210)
T = 80 K

ADSORPTION OF CO ON Pd (210)
O$^+$ and CO$^+$ ESD ION YIELDS
vs.
CO EXPOSURE